

An experimental investigation of electrical conductivities in biopolymers

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Abstract : Some of the gums obtained from plants are found to be conducting biopolymers. Experiments are carried out on some natural gums from both plant and animal origin. In the present work, experimental studies on ion transference number, transient ionic current, thermal analysis, frequency variation of a.c. conductivity and Arrhenius plot of specimens are carried out. The total electrical conductivity of these biopolymers are comparable to that of synthetic polymers doped with inorganic salts. The ion transference number of these biopolymers show their superionic nature of electrical conduction. The overall conduction mechanism seems to be protonic in nature rather than electronic.

Keywords Biopolymers, ion transference number, electrical conductivity

PACS Nos. 81.40.Rs, 82.80.Fk, 72.80.Lc

1. Introduction

Many ion-conductive polymers have been reported so far [1]. It is needless to re-emphasize their future application and scope in tomorrow's technology [1,2]. Recently, Bermudez *et al* [3] have reported that sulfamide and its derivatives exhibit electrical conductivity ($\sim 10^{-3}$ S/cm) at room temperature. The various mechanisms of charge and energy transfer in biopolymers in living biological systems (Cellulose, Collagen, Melanin *etc.*) were studied [4] in details but a comprehensive study on bioproducts as conducting materials is found to be rare. They are commercially cheaper and non-toxic compared to that of synthetic polymer. Following Hummel [5], one can say that popularly known synthetic conducting polymer or its many dopants used to enhance the conductivity, are highly toxic.

In this paper, an investigation on the electrical conductivity of some biopolymers has been done. The preliminary investigation shows that natural gum occurring from some plants of Acacia Genus exhibits electrical conduction properties. It has been found [6] that there exist numerous such gumlike biopolymers within conductivity range $\sim 10^{-3}$ to 10^{-8} S/cm.

Gum Arabica is an important substance in medicine and bacteriology, its chemistry has been well studied [7, 8]. It contains

interior chain $\beta - (1 \rightarrow 3)$ of linked D- galactose units, to which chain comprised of L- arabinofuranose, L- rhamopyranose, and D-glucopyranuronic acid unit are attached. Autohydrolysis of salt free polysacchrde, yields L-arabinose, L-rhamonose and a D- galacto-L- arabinose disaccharide, showing that these entities are linked to the main chain as shown in generalized structure [8], which summarize the structural feature but does not place uniquely the monosaccharide and disaccharide units attached to the chain. The details of it may be found in literature [8, 9].

Beside these plant biopolymers, the various commerical gums extracted from animal ingredients are also found to be very high potent material in this field [10].

The gum Arabica specimen under investigation has a complex molecular structure in which chain of L-Arabinose (24%), L-Galactose (67%) and L-Rhamnose (7%) are interlinked with D-Galacturonic acid ($\sim 2\%$) unit. Its melting point is around 160°C .

A comprehensive experimental study on the gum Arabica along with some preliminary survey on some other biopolymers are presented in this paper. In Section 2 some of the experiments carried out on gum Arabica will be described and section 3 is devoted to the results obtained and discussions.

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2. Experimental procedure

2.1 Preparation of biopolymer specimen

In the present study samples are prepared with Acacia Arabica powder (supplied by LOBA CHEMICAL, Bombay, India) of 98% purity grade by pressing it to make it in the form of a pellet. The powdered gum sample was made as an experimental specimen by preparing a thick viscid bubble free water solution and then allowing it to dry for 3 to 5 days depending on thickness (for 1 mm thick specimen 48 hour is sufficient time).

Finally, the specimen thus obtained is placed in vacuum ($\sim 10^{-2}$ mm of Hg) for at least four hours. In fact, the use of aqueous solution is one of the standard technique in biopolymer sample preparation e.g. hydrogen uranyl phosphate tetrahydrate [11]. The pellet thus produced was sandwiched between two uniform highly polished copper electrodes. The sample prepared by this method may contain trace of free water.

2.2. Detection of conducting ion species

The conducting species in Solid Protonic Conductors SPC [12] may be proton (H^+), hydronium (H_3O^+), hydroxyl ion (OH^-), ammonium (NH_4^+) or dihydronium ($H_5O_2^+$). After a careful experiment by an electrochemical process [12, 13] it has been found that the gum Arabica sample is also a SPC and conducting ion species in it are found to be mostly hydronium (H_3O^+). After a long-duration d.c electrolysis of the sample using porous Cu electrodes (which are prepared from thin copper wire in the form of a dense spiral) it has been found that no hydrogen gas was detected at the cathode rather a loss of the sample weight was recorded. The mentioned loss of weight of the gum Arabica specimen is consistent with Faraday's law of electrolysis and exactly equals to the gain of weight by the anhydrous copper sulphate which is used as a water vapour trap.

2.3. Ion transference number, transient ionic current, bulk electrical conductivity, and Arrhenius plot :

For electrical measurement, polished and clean copper plates were pressed on both surfaces of the biopolymeric film to ensure good electrical contact. The ion transference number of mobile ions (mostly hydronium) in the biopolymer was estimated following blocking electrode method [2], technically known as Wagner's polarization technique [14]. In this measurement, polarization current was recorded as a function of time across a Cu/electrolyte/Cu proto cell and was recorded by a Network 3100 electrometer.

The ionic mobility of mobile species of the gum Arabica specimen is determined by using transient ionic current technique. The sample was subjected to a d.c. electric field across Cu/sample/Cu cell to polarize it. The transient ionic current was then recorded as a function of time by reversing the polarizer electric field. The said reversal is however, done by very simple set-up using a mercury commutator. The current is recorded by a computerised data acquisition system.

The variation of complex impedances and loss angle were also studied for a better information of a.c. conductance of the biopolymer gum Arabica. This measurement was carried between frequency range 1 KHz to 2 MHz by LCZ meter (Model 4192A, HP) and between 1 Hz to 100 KHz by HIOKI LCZ meter (Model 3522, Japan).

The ionic conductivities were measured to depict the Arrhenius plot of the ionic conductivities from 33°C to 125°C for solid specimen by using two probe method. HIOKI 3522 Meter was used for the measurement. The steady volt-ampere characteristics of the solid specimen was also measured using the same set-up.

3. Results and discussions

Figure 1 shows the variation of polarization current as a function of time. The ionic transference number of mobile species in the gum Arabica has been estimated by Wagner's polarization method [15]. The total current i , the initial current at $t=0$, consists of both ionic current (i_{ion}) and the electronic current (i_e), the stabilized current. The ionic transference number is obtained by using standard [2] formula,

$$\tau_{ion} = \frac{i_{ion}}{i} = \frac{i - i_e}{i} \quad (1)$$

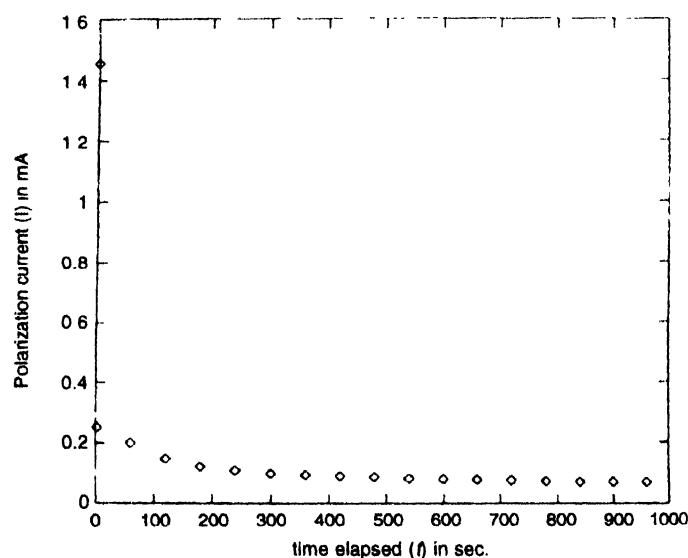


Figure 1. Polarization current (I) in mA vs time elapsed (t) in sec is plotted at room temperature 25°C. The \diamond represent the experimental measured value of the corresponding parameters. Applied potential difference 1.9 Volts and specimen dimensions are of 0.5 mm thickness and 2 cm² in cross-sectional area.

The ionic transference number (τ_{ion}) was found to be $\tau_{ion} = 0.96$. So one may consider that the observed specimen of gum Arabica exhibits ionic character like other solid electrolytes and current occurs mostly due to the motion of the hydronium (H_3O^+). The same has been verified from the mentioned porous electrode experiment on the gum Arabica while passage of electric current. Moreover the observed polarization characteristics of the solid specimen has been found

to be contradictory with earlier results of electrolysis studies [4].

The variation of transient ionic current as a function of time for the gum Arabica sample is shown in Figure 2. Even this very simplistic measurement exhibits a single clear peak which

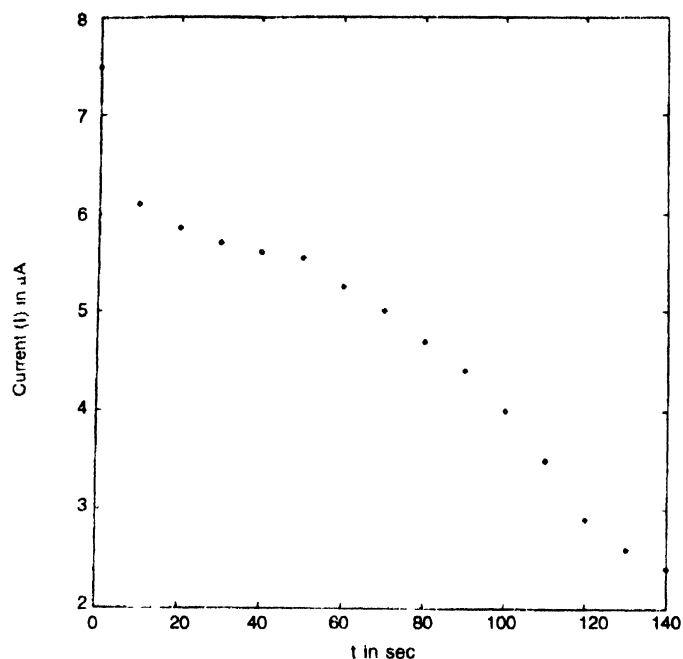


Figure 2. The transient ionic current (I) in μA vs time elapsed (t) in sec is plotted at room temperature 25°C . The \diamond represent the experimental measurement value. Sample thickness = 1 mm, cross-section area = 1 cm^2 and applied p.d. = 1.5 volts.

indicates that the current is due to a single ion species, in this case it is hydronium (H_3O^+) and its ionic mobility (μ) is estimated using the standard formula,

$$\mu = \frac{d^2}{\Gamma V} \quad (2)$$

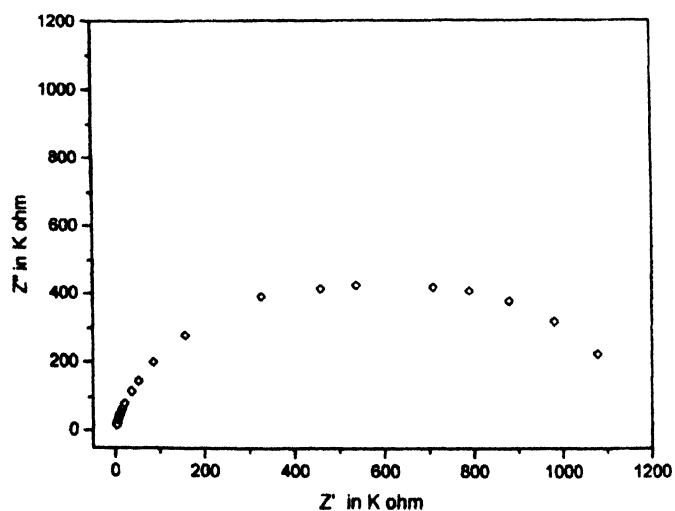


Figure 3. Real part of impedance, $Z'(\omega)$ vs imaginary part $Z''(\omega)$ is plotted between frequency range 1 Hz and 100 KHz at room temperature 25°C . Sample thickness and cross-sectional area are 1 mm and 1 cm^2 respectively. The \diamond represent the experimental points.

where d ($= 1\text{ mm}$) is the sample thickness, Γ ($= 50\text{ sec}$) is the time of flight and V ($= 1.5\text{ Volts}$) is the applied reverse voltage. There exists some uncertainty in the measurement of Γ this is due to lack of very sharp resolution in the determination of the peak in the measurement. However, the error involved in it does not alter the order of magnitude of the estimated value of μ . The value of the ionic mobility obtained from the measurement and using eq (2) is found to be $\mu_{\text{H}_3\text{O}^+} \sim 1.33 \times 10^{-4}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$.

Figure 3 shows a Cole-Cole plot of the variation of impedance with frequency of applied a.c. field. The Cole-Cole plot depicts an important electrical characteristic of any dielectric in general [2]. It shows a semi-circular arc within the measured frequency interval. The centre of the semi-circle is below the real axis. The line joining the left crossing point of the arc with real axis to the centre makes an angle $\sim 20^\circ$ with real axis. The observed single semi-circle in the Cole-Cole plot indicates the existence of single relaxation process of this proton conducting solid.

Figure 4 shows the variation of a.c. electrical conductivity of solid specimen with applied a.c. frequencies at room

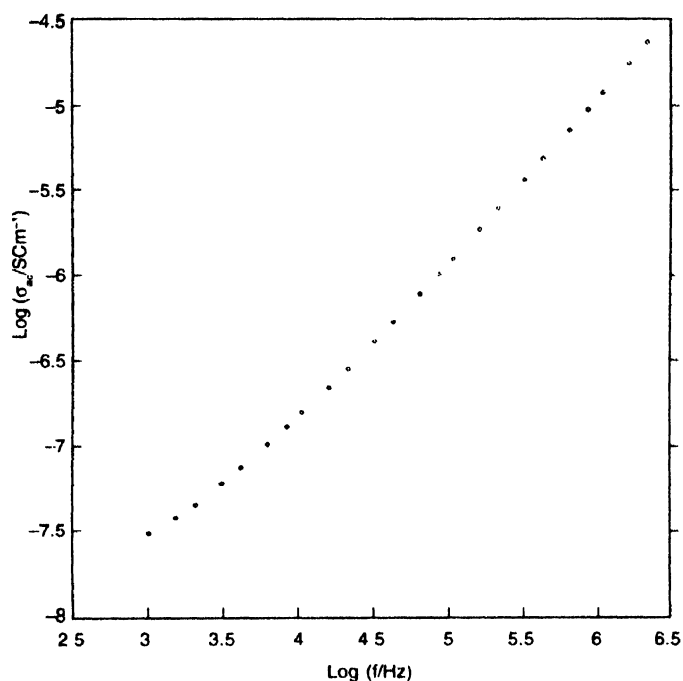


Figure 4. Log electrical conductivities (σ_{ac}) vs log frequencies (f) are plotted at room temperature 25°C . The sample thickness and cross-sectional area are 0.5 mm and 1 cm^2 respectively. The \diamond represent the experimental points.

temperature. The experimental a.c. conductivities have been calculated from measured admittance data following relation,

$$\sigma_{ac}(\omega) = Y' \frac{d}{A} \quad (3)$$

where Y' is the real part of the admittance, d is the sample thickness and A the cross-sectional area of the electrodes. The variation of a.c. conductivity with frequency ω may be described

following equation given by Almond and West [16] and Jonscher's power law viz,

$$\sigma_{\omega} = \sigma_{dc} + K\omega^n \quad (4)$$

or

$$\log(\sigma_{\omega} - \sigma_{dc}) = n \log \omega + \log K, \quad (5)$$

where K and n are material parameters and value of n may be directly estimated from the slope of eq. (5) and a reasonable value of exponent from the Figure 4 which is found to be 0.92 with value of σ_{dc} obtained from extrapolated σ_{ω} to zero frequency and found to be $\sim 1.2 \times 10^{-9} \text{ S cm}^{-1}$. The observed high value of exponential index is similar to that observed for cis-polyacetylene [17] [cis-(CH)_x] and other conducting polymeric system [18] with $\sigma_{dc} \sim 10^{-9} \text{ S cm}^{-1}$ at 295 K and σ_{ω} was found to follow ω^1 variation. It has also been reported [18] that at low frequency σ_{ω} is slightly larger than σ_{dc} . In this present paper the results obtained for σ_{dc} from d.c. experiment are higher than that obtained from extrapolated a.c. data which may be due to the polarization effect and standard deficiencies in two probe method [2].

Figure 5 shows the Arrhenius plot, variation of conductivity with temperatures between temperature range 33°C to 125°C. It is clearly seen from the Figure 5 that the linear nature exists upto the stable temperature range (upto $\sim 100^\circ\text{C}$) of the substance which is also established from the thermal analysis. At

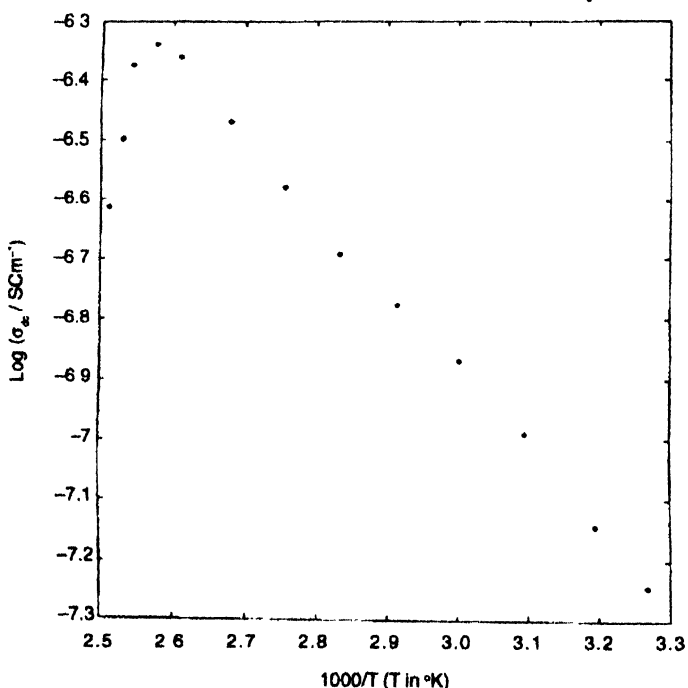


Figure 5. Log. d.c. conductivities (σ_{dc}) [for solid specimen] calculated from stabilized d.c. are plotted against corresponding temperature in the unit of $1000/T$, where T is the temperature in °K. The sample thickness and cross section area are respectively 0.5 mm and 2 cm². The \diamond represent the experimental points. The heating rate was 5°C per minutes. Room temperature 33°C and applied potential difference 1.5 Volts at 1 KHz.

temperatures above 100°C a non-linear behaviour along with a peak in electrical conductivity at around 115°C is observed in the Arrhenius plot. Finally, electrical conductivity tends to decrease above 115°C. This non-linear behaviour is due to the chemical instability during the measurement. In fact, this interesting feature is found to be exhibited by many other SPC [12] and linear Arrhenius plot in the stable temperature range has also been observed for other SPC like H⁺NYS and H⁺NGS [14]. The observed nature of Figure 5 within stable temperature range and the equation may be given by

$$\sigma = \sigma_0 \exp\left(-\frac{E_0}{k_B T}\right) \quad (6)$$

where σ_0 is the pre-exponential factor and E_0 is an activation energy for conduction, which is estimated and found to be 0.17 eV which is comparable to that of other SPCs' and biopolymers like HUP [19].

4. Conclusion

The electrical properties of the conducting biopolymer gum Arabica is similar to that of synthetic conducting polymer doped with inorganic salt and seems to be proton conducting in nature. The gum Arabica is a stable conducting biopolymer upto a temperature 100°C.

Acknowledgments

Authors acknowledge the University Grants Commission, New Delhi, for financial support to this research work MRP (No. F-10-5/98 (SR-I)).

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